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# Electrodeposition of U and Pu on Thin C and Ti Substrates INTDS 2010 Conference Proceedings

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## **Abstract**

Preparation of Pu and U targets on thin natural C (100  $\mu\text{g}/\text{cm}^2$ ) and Ti (2 & 3  $\mu\text{m}$ ) substrates is described. The actinide material of interest was first purified using ion exchange chromatography to remove any matrix contaminants or decay products present in the parent stock solution. The actinide solution was prepared in 0.05 M  $\text{HNO}_3$  with a final aliquot volume not exceeding 100  $\mu\text{L}$  for the deposition procedure. The electroplating cells were developed in-house and were primarily made of Teflon. The source material deposited ranged from 125 to 400  $\mu\text{g}/\text{cm}^2$ . It was determined that multiple layers of U and Pu were required to produce thicker targets on Ti. Plating efficiency was greatly affected by the cell volume, solution aliquot size, pre-treatment of the foils, solution mixing during plating, and the fit of the electrode contact with the target substrate. The final procedure used for deposition is described in detail.

## **1. Introduction**

Production of thin actinide targets is essential for determining various nuclear parameters associated with decay and fission events. The deposition layer of target material must be homogeneously distributed with a thickness relative to the type and efficiency of the reaction under observation and the beam (if applicable) characteristics. As an example, transactinide studies require thicker targets to produce sufficient product for study but still be able to withstand extended heavy ion beam bombardment over long time periods [1], while alpha spectrometry sources require a thin layer of material to minimize energy losses within the deposition [2]. Molecular deposition of actinides from organic media, such as isopropyl alcohol (IPA) is preferred for thin target production because of the relatively high plating efficiency and uniformity of

deposition [3-5]. In this work, targets were prepared for neutron and light-ion bombardment experiments to examine capture cross-section measurements, surrogate cross-sections, and fission neutron spectra for various U and Pu isotopes. The target backing materials were thin C (60 to 100  $\mu\text{g}/\text{cm}^2$ ) or Ti (0.002 & 0.003 mm thickness, rolled) foils and the desired actinide deposition thickness was 125 and 400  $\mu\text{g}/\text{cm}^2$ , respectively. The C foils presented a unique challenge due to the fragile nature of the foil. The Ti backed targets needed to be double-sided with uniform deposition over a large area (13  $\text{cm}^2$ ). The plating cells designed in-house to produce these targets are described.

Actinide target fabrication for cross-section measurements requires the use of high purity actinide salts. In this work, the parent actinide solutions are purified by ion exchange chromatography to remove decay products and other potential matrix contaminants. The parent solutions were in HCl or  $\text{HNO}_3$  prior to purification and the primary contaminants of concern were Th and U. A detailed description of the purification chemistry is provided.

## **2. Experimental**

### **2.1 Chemical Purification of U and Pu Salts**

Ion exchange chromatography was used to purify both U and Pu salts prior to electrodeposition. The U material was dissolved in 8 M  $\text{HNO}_3$ , and was loaded onto a pre-conditioned anion exchange resin (Bio-Rad AG-1-X8, 100-140 mesh) column. Under these conditions, U passes through the column while Th and some other daughter products were retained. The column was rinsed with several column volumes of 8M  $\text{HNO}_3$  and the eluate collected in a glass centrifuge tube. The solution was evaporated to dryness in a water bath, and converted to a chloride salt using HCl. The salt was reconstituted in 9M HCl, which was loaded onto a separate anion exchange resin (AG-1-X8, 100-140 mesh) column. The column was rinsed with several column volumes of 9 M HCl to remove residual Th, then the U eluted with 0.1 M HCl. A few drops of concentrated  $\text{HNO}_3$  were added to the purified U solution during evaporation to convert to the nitrated salt form. The salt was re-dissolved in 100 to 500  $\mu\text{L}$  of 0.05 M  $\text{HNO}_3$  and the solution assayed to determine the final volume required for target production.

The Pu salt was dissolved in a concentrated HCl/HI mixture and evaporated to dryness. The residue was reconstituted in concentrated HCl with a few drops of concentrated  $\text{HNO}_3$ , then evaporated to dryness again. These steps were repeated twice, and Pu

was precipitated from HCl using NaOH. The precipitate was redissolved with a minimum volume of 9 M HCl and a few drops of concentrated  $\text{HNO}_3$ . The solution was loaded onto a pre-conditioned anion exchange resin (AG-1-X8, 100-140 mesh) column and rinsed with 9 M HCl. Plutonium was retained under these loading conditions, while the daughter products and other contaminants were eluted from the column. A concentrated HI/ 10 M HCl (1:12 ratio by volume) eluent was used to remove Pu from the column. The solution was collected in a glass centrifuge tube and evaporated to dryness in a water bath. The salt was reconstituted in a minimum volume of 8 M  $\text{HNO}_3$  and a drop of saturated  $\text{NH}_4\text{NO}_2$  was added to adjust to the  $\text{Pu}^{4+}$  oxidation state. The solution was loaded onto a separate pre-conditioned anion exchange resin (AG-1-X8, 100-140 mesh) column and additional 8 M  $\text{HNO}_3$  used to rinse the column. The resin column was converted to the  $\text{Cl}^-$  form using 9M HCl, then Pu eluted with concentrated HI / 10M HCl (1:12 ratio by volume). The Pu was taken to dryness with the addition of a few drops of concentrated  $\text{HNO}_3$  to convert to the nitrate salt form, dissolved in a minimum amount of 0.05 M  $\text{HNO}_3$  and then assayed to determine the aliquot size needed for the desired target thickness.

## **2.2 Target Production**

### **2.2.1 Electrodeposition on Thin C Foils**

An electroplating assembly was designed to accommodate a 60 to 100  $\mu\text{g}/\text{cm}^2$  C foil mounted on an Al support frame (Figure 1). The base (1) and clamp plates (6) are Al and the chimney (5) and support plate (2) are Teflon. A Viton o-ring (4) was used to maintain the seal between the chimney and pre-mounted target support frame (3). Two alignment rods in the base plate positioned the chimney onto the target frame so that the amount of the frame exposed during plating was minimized. A milled slot in the Teflon support plate accommodated the Al target frame. The assembly was compressed using four pan head machine screws, which were initially pre-tensioned across the diagonal and then rotated half turns sequentially until the assembly was locked in place. The plating power supply (GW Instek model GPR-30H10D, 300W) operated in a constant current mode (4 mA) and the leads were attached to the Pt wire anode and the Al target frame. The Pt wire had a small coil at the end and was suspended just above the substrate to promote even deposition of the actinide.

The carbon foil was floated off the glass slide onto an Al target frame using distilled water, and then allowed to dry at room temperature overnight. A second target frame of the exact same dimensions was coated with a fine spray of organic adhesive (3M 77-Multipurpose Adhesive) and the two target holders were pressed together. The C foil became affixed to the new target frame. This method was developed as an alternative to direct pickup from the carbon slides. When trying to lift the carbon foils directly from the glass slides they would shatter or tear with almost 100% failure. The 60  $\mu\text{g}/\text{cm}^2$  C

targets were very fragile and ruptured easily both before and during plating using this mounting technique; therefore, only the  $100\text{ }\mu\text{g}/\text{cm}^2$  C foils were prepared for cross section studies. The loaded target support frame was slid into the milled section of the Teflon plate. This motion evenly distributes the lateral force while minimizing the perpendicular force on the foil to help prevent rupture. Once assembled, the deposition cell was pre-treated with IPA (approximately half the chimney volume) to check for leaks. An aliquot of the purified actinide solution was added to the assembled cell and the solution was mixed with a transfer pipette prior to deposition. A deposition time of 1 hour was used for both U and Pu target fabrication. At the end of the plating process, the remaining IPA solution was removed from the cell with a transfer pipette and the cell was disassembled. The Al target frame was pushed horizontally across the Teflon support plate until the C foil was completely exposed on both sides, then the Al frame was placed on edge into a plastic 50 mL centrifuge tube to dry. The Al frame fit securely into the tube and prevented surface contact with the C foil. No heat was applied to the foil post deposition due to the fragile nature of the backing material.

### **2.2.2 Double-Sided Electrodeposition on Thin Foils**

An example of the plating cell used for deposition of actinides on both sides of a metal substrate is provided (Figure 2). The blocks were milled from Teflon and the electrodes were Pt (25.4 x 25.4 x 0.051 mm). The Ti target foil was positioned using the grooves milled into the two inner Teflon blocks and held in place by o-rings. The grooves allow for position reproducibility should multiple layers be required to achieve the desired target thickness. The outer and inner Teflon blocks were pre-assembled with the Pt anodes prior to loading the target foil. Once the foil was positioned on one half of the cell, a Pt cathode was placed so that electrical contact was maintained between the power supply and the foil. The second half of the cell was positioned and fixed in place with cap screws. The power supply was set at a constant current ( $3\text{ mA}/\text{cm}^2$  target) and the two anodes were connected by a jumper cable. Solution mixing was kept constant using a peristaltic pump (ISMATEC Reglo-Digital, 100 rpm) throughout the deposition procedure.

Once the cell was assembled, IPA and a 100  $\mu\text{L}$  aliquot of 0.05 M  $\text{HNO}_3$  were added to the solution wells and mixed for 30 minutes. This process cleaned the substrate prior to plating. The cleaning solution was removed from each cell and the IPA and actinide solution aliquot were added. The solutions were equilibrated for 30 minutes, followed by a 1 hour deposition. The pump was used to remove the remaining plating solution and the cell was disassembled. The target foil was placed in a glass evaporation dish for secondary containment and was heated on a hot plate for at least 1 hour. The deposition thickness was determined by gamma spectrometry, assuming equivalent plating efficiency.

### 3. Results and Discussion

#### 3.1 Thin C Targets

The thin natural C targets presented a unique production challenge. The material was very fragile, with a 40% rupture rate during plating. Most tears occurred at the interface between the target support and the C foil. The foils were mounted to the target frames using a floating technique, which created a rippled surface (Figure 3) and may have contributed to the failure of the films. The plated U targets were bright yellow, with the material concentrated along the ridges in the foil (Figure 4, top). Plutonium deposition was more homogeneously distributed across the surface of the foil (Figure 4, bottom) and was black in appearance. The targets were not quantified by alpha spectrometry; however, the remaining IPA/HNO<sub>3</sub> solution was evaporated to near dryness and then assayed to determine the amount of actinide remaining in solution. A near quantitative transfer of 125 µg/cm<sup>2</sup> of either U or Pu on target was achieved in a single plating using this process.

#### 3.2 Double Sided Targets

Ti foils were used for double-sided target production. These foils did not rupture during plating, and a thickness of 400 µg/cm<sup>2</sup> (per side) was produced with two successive depositions. For U targets with a 4 cm diameter plated area, the first deposition resulted in a nominal thickness of 300 µg/cm<sup>2</sup>. The foil was baked on a hot plate at moderate heat, to eliminate any concern for burning of the Ti foil, for several hours, then assayed by gamma spectrometry. The foil was reloaded in the Teflon cell, using the alignment grooves to aid positioning of the foil, and the procedure was repeated with the final 100 µg/cm<sup>2</sup> of U dissolved in a minimum volume of 0.05 M HNO<sub>3</sub> (< 100 µL). The surface of the target appeared to be smooth with an iridescent sheen where the U was deposited (Figure 5). A total of eleven foils have been produced by this method with similar results.

A foil containing 400 µg/cm<sup>2</sup> (per side) of Pu was produced in four successive depositions. The first three deposited a total of 100 µg/cm<sup>2</sup> (per side). After each deposition, the foil was baked for several hours, placed in secondary containment and assayed by gamma spectrometry. After each assay, the secondary container was checked for activity. The amount of activity present in the container was significant compared to the U targets, suggesting decreased mechanical stability of the plated material. The initial design of this cell was a simple modification of the U target plating cell with the diameter of the plating area reduced from 4 cm to 7 mm. Due to the flexibility of the Teflon material and the distance to the clamping screws, the Pt cathode fit very loosely in the apparatus. The inner walls of the cell were re-fabricated, relocating the plating area to within 2 cm of the top of the cell and reducing the fluid volume. The

electrodes were re-fitted into the modified cell. The target was reloaded into the cell and an aliquot volume equivalent to  $300\text{ }\mu\text{g}/\text{cm}^2$  and IPA were added to each solution well. After the final deposition, gamma assay estimated a  $500\text{ }\mu\text{g}/\text{cm}^2$  thickness on each side of the target. The extra deposited material was assumed to be from the contaminated Pt anodes that were used in the previous design and were not cleaned prior to the final deposition. The final target was black in appearance and produced far less contamination in the secondary container, indicating better adhesion to the Ti substrate. More Pu targets will be produced in the future, but due to the activity of the desired deposit, the work will have to be performed in a glovebox. This has necessitated a new design for the center clamping mechanism, as there is not sufficient dexterity to handle the cap screw, washers, and nuts with the current design.

#### **4. Summary**

The chemistry and electrodeposition cells described in this work are suitable for producing high purity actinide targets on thin C and Ti foils. The double-sided cell design is currently being modified for a glovebox environment so that other actinides of interest can be electrodeposited on these films. The electrodeposition cell for the thin C foils produced a fairly homogenous distribution of both Pu and U; however, the process needs to be optimized to reduce the failure rate (i.e. target tearing). A separate technique is being developed for mounting the C foils on the Al frames. These foils will be tested in the electrodeposition cell prior to any structural modification.

#### **5. Acknowledgements**

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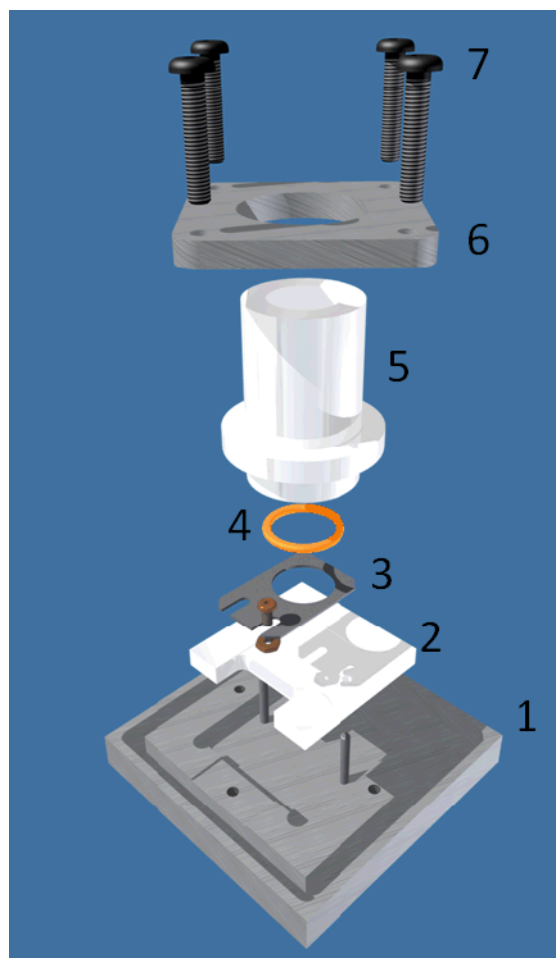


Figure 1. Electrodeposition cell for actinides on thin C foils.

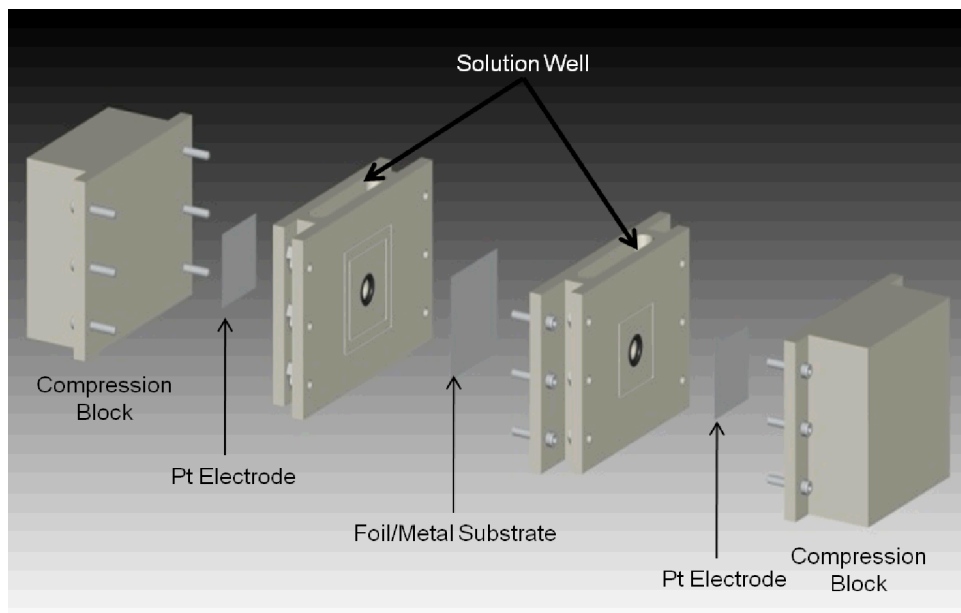


Figure 2. Schematic of the double sided electrolytic cell.

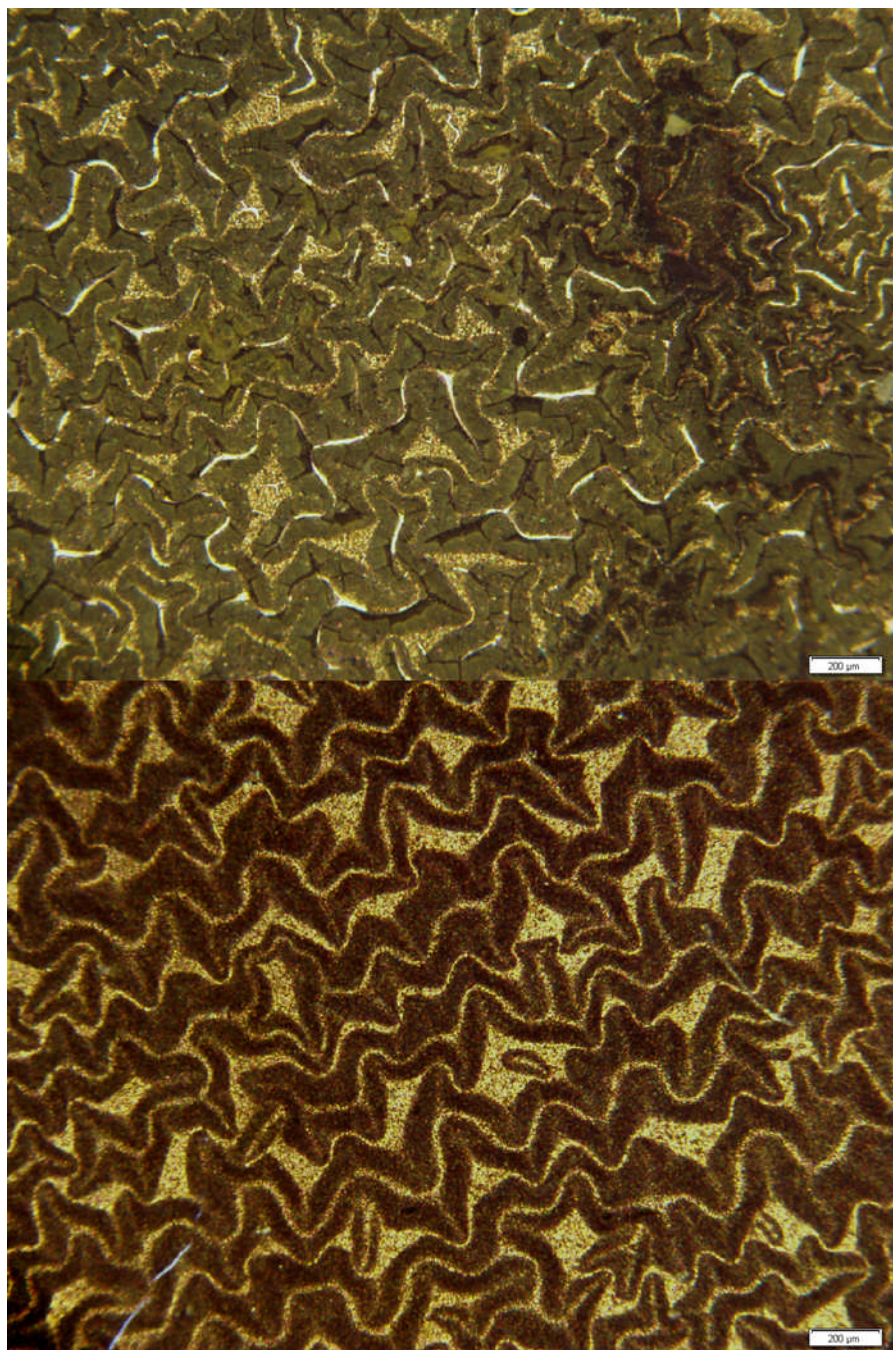


Figure 3. Surface of thin C foils after plating U (top) and Pu (bottom). Images were obtained with a petrographic microscope. Scale bar is 200  $\mu\text{m}$ .



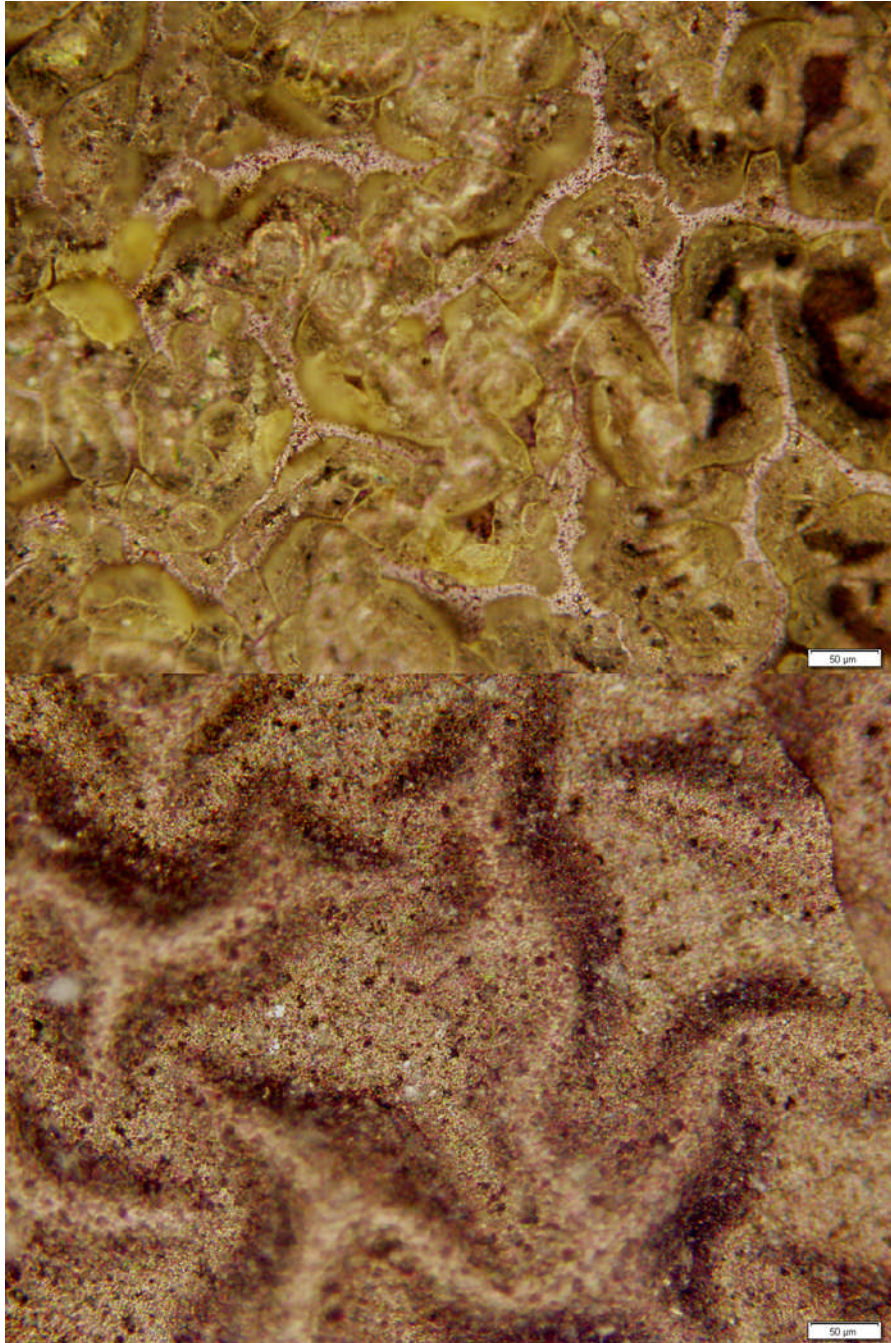


Figure 4. Uranium (top) and Pu (bottom) deposition on thin C-foils. Images were obtained with a petrographic microscope. Scale bar is 50 μm.

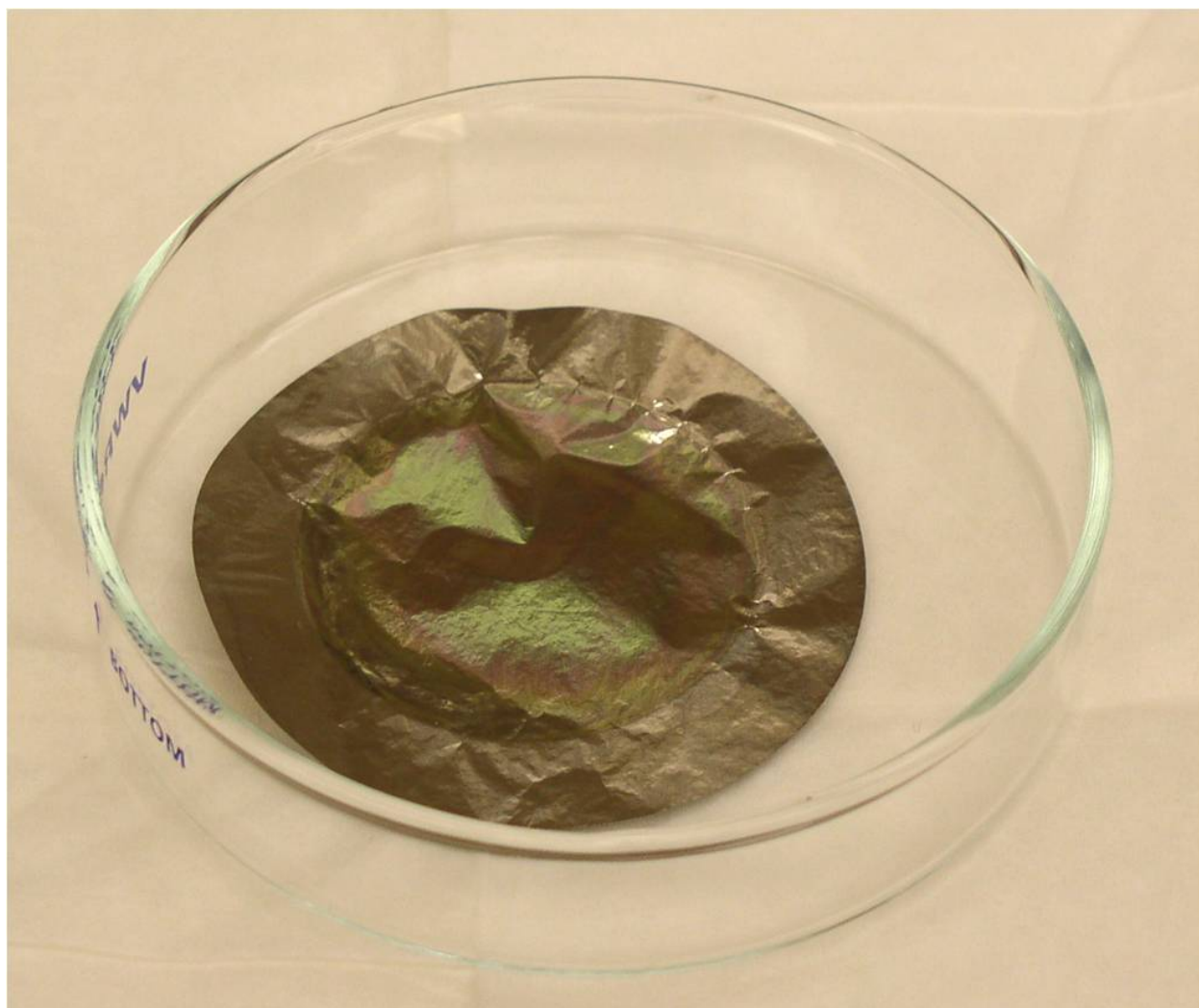


Figure 5. Thin Ti foil with  $400\text{ }\mu\text{g}/\text{cm}^2$  of U deposited on the surface.

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